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Development of new photovoltaic devices based on multi wall carbon nanotubes and nanoparticles

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14. ABSTRACT

We have demonstrated that multiwall carbon nanotube (CNT) films decorated with noble metal nanoparticles can be used to generate photoelectric current from visible and near ultraviolet light. It is also interesting to note that some insights into the photo-generation mechanism can be inferred comparing the experimental results to the theoretical density functional theory simulations. A mechanism of photo charge generation is described in which the presence of the noble metal particles on the tubes deeply modifies the electronic properties of the CNT hybrid and makes available additional charges that are involved in the photo generation process. The main consequence is that a remarkable increase in the photocurrent response is registered in all the photon spectral range studied. The new kind of Graetzel-like solar cell device was built without dye and TiO2, showing an IPCE up to 20%.

15. SUBJECT TERMS

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Motivations:

Recent studies have highlighted the possibility of achieving high efficiency by using carbon nanotubes solar cells instead of conventional semiconductor materials (Si, GaAs, etc..). In particular, the one-dimensional nature of nanotubes can offer great advantages due to the high active surface available for absorption of photons that can lead to a major electric power generation. The CNTs exhibit so remarkable electronic and structural properties that they now constitute the building blocks in several different nanoscale devices. Recently, CNTs have been incorporated in a variety of composite materials with even more attractive properties and possible applications. In fact, the extended active surface area, good conductivity and thermal stability of the CNTs, have been exploited by interfacing them with a large variety of entities ranging from inorganic, polymers and biomolecules. These CNT base hybrid systems exhibit new functions that originate from the cooperative effect of the distinctive properties of the two class materials used, the CNTs and the nano-objects, and have found a broad range of applications. In this research field, an interesting class of derivatives rises from the controlled deposition of metal nanoparticles (NPs) on the CNTs.

Introduction:

The focus of our experimental research has concerned the optical and electronic properties of metal nanoparticles–MWCNT composites, in view of extensive application both in electrochemical and solid state operating light energy conversion devices. The direct deposition of the metal atoms on the CNT by means of in-situ thermal evaporation is the physical method of our choice. In fact, this method offers some advantages with respect to the chemical routes. As an example, it does not require CNT surface modification and is a single-step process with a reduced number of parameters to be controlled. Large yields of uncontaminated CNT–nanoparticle composites can be produced with a good control of particle size. Consequently, heterostructures are readily available for developing multifunctional nano-systems with minimal post-synthesis processing. In this project, we demonstrated that the 'in situ' thermal deposition of Cu, Au and Ag on the MWCNT films produces metal NPs on the tubes outer wall and gives large yields of uncontaminated CNT based composites. In addition, the light energy conversion response of such CNT composites is studied with photo electrochemical measurements. The electronic process that regulates the optical response of the composites is drawn from the experimental and the theoretical results reported, proving that these heterostructures are readily available for applications both in electrochemical and solid state operating light energy conversion devices.

The scientific background of this project is based on the experience of the proposers regarding growth of carbon nanotubes through a CVD (Chemical Vapor Deposition) process, the characterization of carbon nanotubes (both single and multiple wall) and also on the observations of high photocurrent measured in cell photo-electrochemical cell produced from a sample of carbon nanotubes decorated with nanoparticles of copper (about ten times the photocurrent measured for samples of carbon nanotubes without external decoration) (1). Additionally, the main result of our measurements is a photo-current with an efficiency of 7% IPCE (Internal Photo Current Efficiency) for multi-walled carbon nanotubes (2). This result was obtained, for the first time in the world, in our laboratory of Rome Tor Vergata University.

Development of the work:

The whole project of our research Unit has been developed as follows:
a) synthesis, structural and electronic study of multi wall carbon nanotubes;
b) realization of hybrid carbon based nanomaterials through the decoration with nanoparticles of Cu, Au and Ag,
c) The nanoparticle-carbon nanotube films were characterized by photo-electrochemical measurements in a standard three electrode cell.
d) production of samples of large size (5cm x 5cm) of samples as prototypes for solar cells.

The achievements of the above objectives entails the characterization of nanostructures by using different morphological, structural, electronic and optical techniques. This has been obtained through:
a) CVD (Chemical Vapor Deposition) fabrication of carbon nanotubes (multi wall with variable number of inner shells, defects, dimension of the catalysts Fe nanoparticles) with high degree of purity. Carbon nanotubes have been directly grown on Si(111) substrates;
b) The structural, electronic and transport properties of the nanostructures obtained has been investigated by using electron spectroscopies and microscopies (SEM, TEM, EELS and XPS).

The synthesis of the metal NP-MWCNT composites was carried out into two subsequent steps: the growth of CNT film followed by in-situ metal deposition that generated the NPs. In brief, Fe (1.00+0.01nm, nominal thickness (NT)) catalyst was thermally deposited on a cut piece of Si(111). The carbon nanotubes were grown by thermal chemical vapor deposition (CVD) using acetylene (C_2H_2) gas atmosphere (200 sccm, 12 Torr) as carbon precursor while keeping the Si-Fe sample at 750 C, for 10 min. The second step of the synthesis was the CNT films decoration. This task was performed in-situ under vacuum condition (10-8 Torr, base pressure) through a thermal evaporation process from a tungsten crucible, one for each metal, performed at the same deposition rate of 0.5 A /min. Au, Ag, and Cu were the metals used in the experiment. A set of three samples for each metal was synthesized simply by varying the evaporation time. The correspondent NT deposited was 0.20, 0.50, and 3.0 nm, respectively. Field emission gun scanning electron microscopy (FEG-SEM, Leo Supra 35) was used to collect images directly on the MWCNT samples. Figures 1(a)– 1(c) report a collection of typical SEM images obtained on the MWCNT film after 3.0nm NT deposition of Au (a), Ag (b), and Cu (c), respectively. From the images, it can be noticed that the metals deposition formed discrete NPs on the CNT outer wall with a uniform dispersion (see Fig.2), as expected from these metals (3).

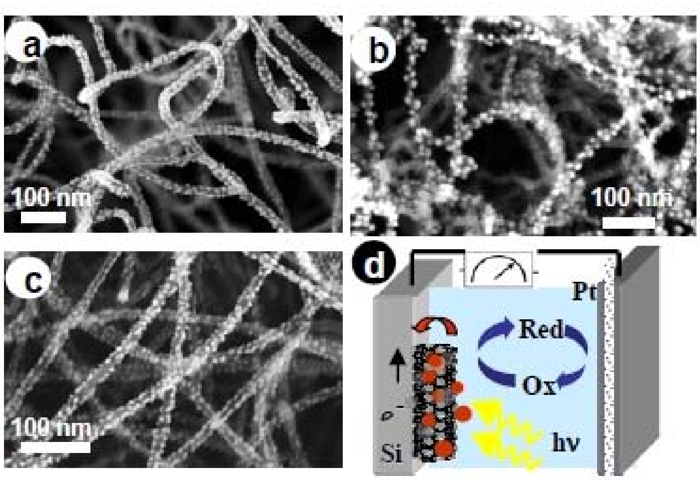

FIG. 1. SEM images of the MWCNT-based devices. (a) Typical image of the MWCNT film decorated with Au (a), Ag (b), and Cu (c) NPs, respectively. Images ((a)-(c)) have been obtained after thermal evaporation of 3 nm of metal NT. Scale bar is 100nm in all images. (d) Schematic illustration showing the three electrodes cell set-up and the mechanism of the charge formation and collection upon light irradiation (solution 0.5M KI and 0.01M I2 in acetonitrile, Ecell=12 mV).

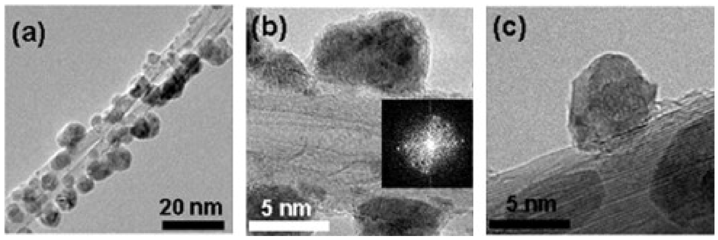

Fig.2 - Collection of high resolution TEM images of Cu-MWCNT samples. (a) Focus on a tube wall and many Cu NPs; (b) Cu NP and the FFT inset; (c) aggregated NPs on a tube wall. From Scarselli et al.(3).

The MWCNT-based device photoresponse was measured with a conventional three-arm photo-electrochemical cell, using platinum (Pt) wire as the counter electrode and a saturated calomel electrode (SCE) as the reference electrode. A 0.5M KI and 0.01M I2 in acetonitrile solution was used as the electrolyte, the applied potential in all measurement being 12mV, as shown in the scheme of Fig. 1(d). A 200W Xe lamp (Osram) equipped with a monochromator a) was employedas the excitation source (k>300 nm) and a PG-310 potentiostat (HEKA Elektronik, Lambrecht, Germany) was used for controlling the applied potential and photocurrent intensity measurements. The intensity of the light at the excitation wavelength near the electrode surface (50mW/cm2) was determined by azobenzene actinometry.13 The photoresponse of the samples was evaluated in terms of incident photon-to-charge carrier generation efficiency (IPCE)14 directly from the time traces of the on-off irradiation cycles, like those reported in Figure 3.

The photo-response from the three sets of samples is reported in terms of IPCE in Figures 3(a)–3(c) for each metal and nominal thickness used. The value can be compared to that acquired from the bare MWCNT film. Starting from Au–MWCNT samples of Figure 3(a), it can be noticed that for 0.2 nm and 0.5 nm NT, the signal is greater than that from MWCNTs, while that obtained from the 3 nm NT sample is lower in all photon spectral range studied. The maximum in the IPCE reaches 10.7% at around 370 nm for 0.5 nm NT sample compared to that of the MWCNTs at the same wavelength that is 5.9%. Although the best photoresponse is concentrated around the ultraviolet energy range, it remains greater than that of the bare MWCNT film in all spectra. The maximum IPCE value from the bare MWCNT samples in Fig. 3 varied from 5.7% to 6.6%. This can be ascribed to structural fluctuations in the CNT that influenced the optical response, as we have already reported. A similar trend in the IPCE curves has been obtained from the MWCNT samples decorated with Ag and Cu, Figs. 3(b) and 3(c), respectively. Again the observed trend indicates that a moderate deposition of metal on the tube walls increases the photoresponse. In the case of Ag, the signal grows up to 19.4% around 370 nm, that is three times higher than that of the CNT that is only

5.7%. No appreciable effect was observed for 3 nm NT. Finally, Figure 3(c) collects the IPCE from the Cu-MWCNT samples. The IPCE evaluated from the Cu-MWCNT film reaches a maximum of 15.4% at 360 nm compared to that of the MWCNT of 6.6% for 0.2 nm NT. The maximum IPCE value is located in the ultraviolet spectral region, confirming the results reported in similar recent experiments (3).

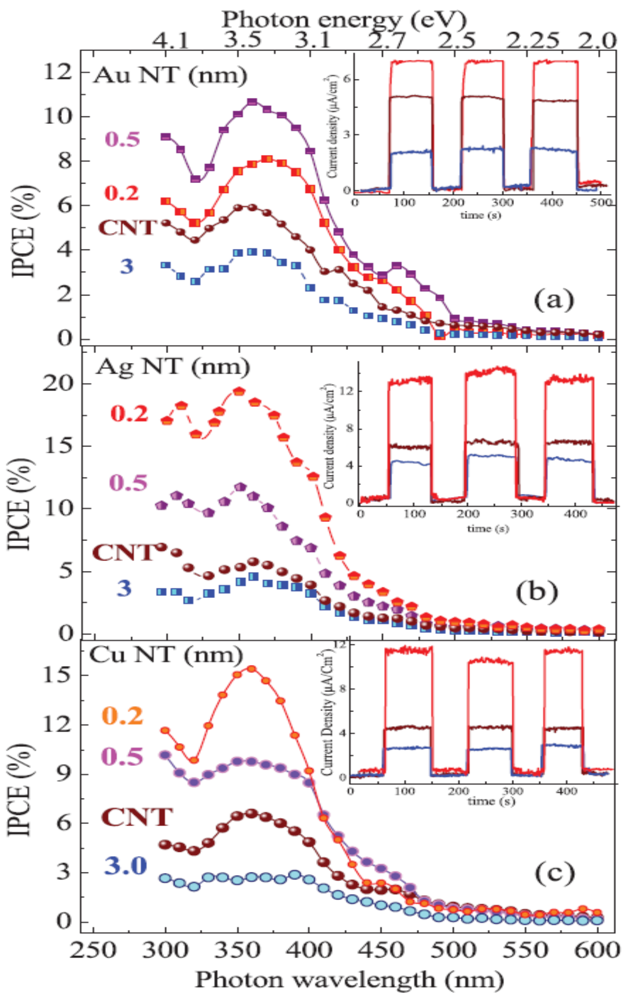

Fig.3 (a) Schematic showing the three electrodes cell set-up and the mechanism of the charge formation and collection upon light irradiation (0.5 M KI and 0.01 M I2 in acetonitrile solution, Ecell = 12 mV). (b-d) Evaluated results of the IPCE from the three MWCNT-hybrids and the bare MWCNT film as a function of the incident photon wavelength. (b) Au-MWCNT, (c) Ag-MWCNT and (d) Cu-MWCNT. The line color corresponds to the same NT (red for 0.2 nm, violet for 0.5 nm and blue for 3 nm) used for all set of samples. From Scarselli et al.(4)

All samples showed a prompt response to incident light and the current signal is anodic in character. This means that the electrons flow from the metal NP/MWCNT composite to the collecting auxiliary electrode, as described in Fig. 3(d). It is important to underline that these measurements are very sensitive to the surface process, and the observed signal is produced and collected only at the metal MWCNT film-Si interface. In fact, photocurrent measurements performed on the Si substrate before and after the Fe catalyst deposition did not show any photocurrent response (data not shown). In addition, all the three metal NP-MWCNT composites studied exhibit a line shape that closely resembles that of the bare MWCNTs. The observed increase in the photocurrent signal that we obtained at the macroscopic level suggests the existence of a microscopic electronic mechanism enhancing the photocurrent efficiency. In particular, the observed trend (Figs. 2(a)–2(c)) suggests that in the presence of metal NPs, additional charges are made available and efficiently collected at the electrode. This implies that a charge transfer might have occurred at the microscopic level in the entire hybrid system that involved both the CNT and the particles before light excitation. A charge transfer process for a metal single wall carbon nanotube (SWCNT) in close contact with a linear chain of Cu atoms was theoretically described by Kong et al.(5) The authors predicted an efficient electron transfer from the Cu atom in the chain located on top of the C atom in the tube. An increase in the density of states of the C atom was also found, thus, confirming that this simple hybrid system showed electronic properties remarkably different from those of the two starting constituents.

In order to shed some light onto the microscopic mechanism that regulates the increased photocurrent, we have calculated, for graphene decorated with Au, Ag, and Cu NPs, the geometry and the electronic properties of the composite system for three different NPs size. Figure 4(a) reports the result of the simulation of a Cu NP (d=0.8 nm) on top of a graphene layer where the charge depletion and accumulation areas have been determined. A similar trend was also found for Au and Ag.

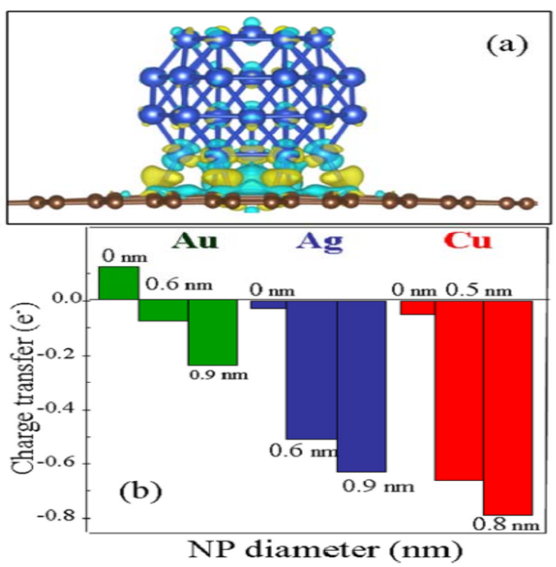

Fig.4 - DFT (Density Functional Theory) calculations for a simplified CNT/NP hybrid system, here, modelled by metal clusters on top of a graphene layer. (a) Simulation of a Cu NP (d=0.8 nm) on top of a graphene layer. Charge depletion areas are shown in light blue and charge accumulation areas in yellow. (b) Charge transfer from the NP to the graphene substrate (when<0) and vice-versa (when>0). The charge transfer from the metal to the graphene substrate increases with increasing NP diameter. 0 diameter NP refers to 1 atom cluster. From Scarselli et al. (4).

In conclusion, we have demonstrated that MWCNT films decorated with noble metal NPs can be used to generate intense electric currents upon photon absorption in the visible and near ultraviolet region. Insights into the photogeneration mechanism can be inferred comparing the experimental results to the theoretical simulations. A mechanism of photo-induced charge generation at the interface is described in which the presence of the metal NPs on the tubes deeply modifies the electronic properties of the CNT and makes available additional charges that are subsequently involved in the photo generation process. The main consequence is that a significant increase in the photocurrent response of the NP/CNT composite is registered in all the photon spectral range explored.

In summary:

- we have demonstrated that MWCNT films decorated with noble metal nano-particles can be used to detect visible and near ultraviolet light.

- The detection is based on photo-electrochemical measurements. It is also interesting to note that some insights into the photo-generation mechanism can be inferred comparing the experimental results to the theoretical DFT simulations.

- A mechanism of photo charge generation is described in which the presence of the noble metal particles on the tubes deeply modifies the electronic properties of the CNT hybrid and makes available additional charges that are involved in the photo generation process.

- The main consequence is that a remarkable increase in the photocurrent response is registered in all the photon spectral range studied.

- The new kind of Graetzel (DSSC, Dye Synthesized Solar Cell) built without Dye and TiO2, devices showed a IPCE up to 20%.

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